

Zirconium Phosphates of Variable Dimension Templated by Ethylene Diamine: Crystal Structures of 1-D $[\text{enH}_2][\text{Zr}(\text{HPO}_4)_3]$ and 2-D $[\text{enH}_2]_{0.5}[\text{Zr}(\text{PO}_4)(\text{HPO}_4)]$

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Hydrothermal reaction of $\text{Zr}(\text{OPr})_4$ with H_3PO_4 in the presence of ethylene diamine and HF yields three crystalline phases; the 1-D $[\text{enH}_2][\text{Zr}(\text{HPO}_4)_3]$, **1**, which can grow as needles over 1 mm in length, the 2-D $[\text{enH}_2]_{0.5}[\text{Zr}(\text{PO}_4)(\text{HPO}_4)]$, **2**, which is found as thin plates, and the previously reported fluorinated 3-D open-framework compound $[\text{enH}_2]_{0.5}[\text{Zr}_2(\text{PO}_4)_2(\text{HPO}_4)\text{F}] \cdot \text{H}_2\text{O}$, **3**. The 1-D phase is the first of its type, with each Zr linked to neighboring metal atoms in the chain by three bridging phosphate groups via Zr–O–P–O–Zr linkages. Its crystals are monoclinic, space group $C2/c$, $a = 8.996(3)$, $b = 15.373(5)$, $c = 9.582(4)$ Å, $\beta = 102.97(2)^\circ$, $V = 1287(1)$ Å³. Compound **2** is orthorhombic, space group $Pnmm$, $a = 24.087(4)$, $b = 5.381(1)$, $c = 6.660(1)$ Å, $V = 863.0(4)$ Å³. It is related to the ‘double layer’ sheet compound γ -ZrP and its ion exchanged analogues. © 1998

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INTRODUCTION

Metal phosphates have been extensively studied for their potential applications in a number of materials areas, notably the ALPO family as microporous molecular sieves and for their catalytic activity. Certain classes such as the titanyl phosphates have useful nonlinear optical properties. Acidic phosphates also offer possibilities for ion exchange and solid-state conductivity properties (1). The work of Clearfield and others has established the rhombohedral family $[\text{Zr}_2(\text{PO}_4)_3]^-$ (2) and the lamellar zirconium orthophosphates as important systems for studies of this type (3–6). The lamellar phases include α -ZrP $[\text{Zr}(\text{HPO}_4)_2] \cdot \text{H}_2\text{O}$ (3), the anhydrous β -form, and γ -ZrP $[\text{Zr}(\text{PO}_4)(\text{H}_2\text{PO}_4)] \cdot 2\text{H}_2\text{O}$ (5).

Organically functionalized phosphonate esters (RPO_3) have been used in place of (HPO_4) groups and may become incorporated into lamellar phases much related to the orthophosphates, which may have interesting and novel materials properties (7). Despite this and the discovery over

the past 20 years of many organotemplated inorganic materials, including a wealth of such structures for the aluminophosphates, until recently there were few examples of organically templated zirconium phosphates.

However, in 1995, a 1-D double-stranded polymer, $[\text{enH}_2]_{1.5}[\text{Zr}(\text{PO}_4)(\text{HPO}_4)\text{F}_2]$, was synthesized from a predominantly nonaqueous alcoholic solvothermal route (8). More recently, the first 3-D microporous zirconium phosphate containing an organic template, $[\text{enH}_2]_{0.5}[\text{Zr}_2(\text{PO}_4)_2(\text{HPO}_4)\text{F}]$, **3** was characterized (9). Once more the template is ethylenediammonium, (enH_2); the compound is fluorinated and like the 1-D phase has terminal Zr–F bonds.

Herein we report further studies on the organically templated phases which result from use of ethylene diamine in the system $\text{Zr}(\text{OPr})_4/\text{H}_3\text{PO}_4/\text{HF}/\text{en}/\text{H}_2\text{O}$ and the discovery of two new low-dimensional zirconium phosphates, 1-D $[\text{enH}_2][\text{Zr}(\text{HPO}_4)_3]$, **1**, and 2-D $[\text{enH}_2]_{0.5}[\text{Zr}(\text{PO}_4)(\text{HPO}_4)]$, **2**. The first we believe to represent a new fundamental structural type; the second is a double-layered sheet material closely related to γ -ZrP. In addition, a high yield preparation of excellent quality crystals (Fig. 1) of **3** was found using $\text{Zr}(\text{OPr})_4$ as the zirconium source, rather than ZrOCl_2 , as reported previously (9).

EXPERIMENTAL SECTION

Synthesis of **1** and **2**

A gel of composition 1.0 $\text{Zr}(\text{OPr})_4$ (0.77 mL): 5.0 H_3PO_4 (85%) (0.73 mL): 2.0 HF (20% soln.) (0.38 mL): 2.0 ethylene diamine (en) (0.33 mL): 60 H_2O (2.5 mL) with an initial pH 5.0 was heated in a stainless steel autoclave at 180°C for 15 days. The product was washed with DI water and organic solvents to give a mixture of amorphous material along with two colorless crystalline components, fine needles of compound **1** (about 15%) (Fig. 1a), and thin plates of **2** (about 25%) (Fig. 1b). EDAX analysis showed the presence of Zr and P but not F in the two crystalline phases. To date, use of

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FIG. 1. Optical micrographs of **1**, **2**, and **3** showing crystal habits consistent with the framework dimensionality. (a) Needles of 1-D $[\text{enH}_2][\text{Zr}(\text{HPO}_4)_3]$ up to 1.5 mm in length; (b) plates of 2-D $[\text{enH}_2]_{0.5}[\text{Zr}(\text{PO}_4)(\text{HPO}_4)]$, typical size 150 μm on edge and 10 μm thick; and (c) rods of 3-D $[\text{enH}_2]_{0.5}[\text{Zr}_2(\text{PO}_4)_2(\text{HPO}_4)\text{F}]\cdot\text{H}_2\text{O}$; Scale bar in the photographs is 200, 100, and 200 μm , respectively.

varied synthesis conditions has not allowed phase-pure preparation of either phase.

Synthesis of **3**

The recently reported compound **3** was synthesized as rod-like crystals of 200 μm dimension (Fig. 1c) in high-yield (about 75% based on Zr) and phase-pure by a slight variation of the above conditions, employing a larger stoichiometry of hydrofluoric acid. The gel composition 1.0 $\text{Zr}(\text{OPr})_4$ (0.77 mL):5.0 H_3PO_4 (85%) (0.73 mL):8.0 HF (20% soln.) (1.47 mL):2.0 ethylene diamine (en) (0.33 mL):120 H_2O (5 mL) with pH 1.5 was heated for a total of 18 days. Phase identification was based on single-crystal structure determination and powder X-ray diffraction. The structure is in close agreement with Ref. (9) and details are available on request from the authors.

^{31}P NMR Spectroscopy

CP-MAS solid-state ^{31}P NMR spectra were recorded on a JEOL 400 MHz instrument and referenced to 85% H_3PO_4 as external standard (downfield shifts positive). Pure samples of **1** and **2** were prepared by manual separation. Compound **1** gave shifts of -8.9 and -14.4 ppm; compound **2** -17.1 and -26.4 ppm, and compound **3** -19.1 and -24.2 ppm.

Crystal Structure Determination of **1**

The compound crystallizes as a minor component of long needles typically >200 μm in length. A specimen $0.2 \times 0.04 \times 0.02$ mm dimension was used. Structure determination details are given in Table 1. Systematic absences were consistent with either space group Cc or $C2/c$ and refined without disorder of the nonhydrogen atoms in the centric space group, in which case the Zr atom is required to sit on an inversion center and one phosphorus P(2) on a two-fold axis. Solution by Patterson method, followed by full matrix least squares refinement for 655 observed data, gave final discrepancy indices of $R = 0.045$, $wR = 0.040$ for 97 parameters and a goodness-of-fit of 1.21. Hydrogen atoms could be located, but were placed in geometric positions with riding constraints. Some disorder of phosphate hydrogens was found. Residual electron densities were $+0.98/-0.75 \text{ e}\text{\AA}^{-3}$. Atomic fractional coordinates and thermal parameters are given in Table 2. Selected bond lengths, angles, and nonbonded contacts are listed in Table 3.

Crystal Structure Determination of **2**

This compound is the major component in the mixture of **1** and **2**. It crystallizes as thin sheets approximately 15 μm thick, and a specimen about $0.15 \times 0.1 \times 0.015 \text{ mm}^3$ was

TABLE 1
Structure Determination Summaries for **1** and **2**

	Crystal data	
Empirical formula	$\text{C}_2\text{H}_{13}\text{N}_2\text{O}_{12}\text{P}_3\text{Zr}$	$\text{CH}_6\text{NO}_8\text{P}_2\text{Zr}$
Color, habit	Colorless needle	Colorless plate
Size (mm)	$0.2 \times 0.04 \times 0.02$	$0.15 \times 0.10 \times 0.015$
System, space group	Monoclinic $C2/c$	Orthorhombic $Pnmm$
Unit cell dimensions		
<i>a</i> (\AA)	8.996(3)	24.087(4)
<i>b</i> (\AA)	15.373(5)	5.381(1)
<i>c</i> (\AA)	9.582(4)	6.660(1)
β ($^\circ$)	102.97(2)	
Cell volume (\AA^3)	1287.0(1.4)	863.0(4)
Formula weight/Z	441.3/4	313.2/4
Density (calc.) Mg/m^3	2.28	2.42
$\mu(\text{MoK}\alpha) \text{mm}^{-1}$	1.29	1.67
<i>F</i> (000)	880	612
	Data collection	
2Θ range ($^\circ$)	3.0–48.0	3.0–50
Index ranges	$-1 \leq h \leq 9$ $-1 \leq k \leq 17$ $-10 \leq l \leq 10$	$-1 \leq h \leq 28$ $-1 \leq k \leq 6$ $-1 \leq l \leq 7$
Unique reflections	992 ($R_{\text{int}} = 3.87\%$)	823 ($R_{\text{int}} = 3.12\%$)
Observed reflections	655 ($F \leq 4\sigma(F)$)	486 ($F \leq 4\sigma(F)$)
Absorption correction	Semi-empirical (psi-scan data)	
Min/Max transmission	0.88/0.99	0.82/1.00
	Solution and refinement	
Number of parameters	97	74
<i>R</i> indices (obs. data)	$R = 0.045$, $wR = 0.040$	$R = 0.043$, $wR = 0.039$
<i>R</i> indices (all data)	$R = 0.084$, $wR = 0.045$	$R = 0.092$, $wR = 0.049$
Goodness-of-fit	1.21	1.21
Largest and mean Δ/σ	0.076, 0.004	1.67, 0.13
Data: parameter ratio	6.8:1	6.6:1
Largest diff. peak/hole	$+0.98/-0.75 \text{ e}\text{\AA}^{-3}$	$+1.15/-1.60 \text{ e}\text{\AA}^{-3}$
System used	Siemens Shelx1t-Plus (Ref. 21)	

used for data collection. The systematic absences indicated one of the relatively uncommon space groups, $Pnmm$ or $Pnn2$. Solution by direct methods allowed structure refinement in the centrosymmetric choice, with no disorder for the nonhydrogen atoms. Once more the hydrogen atoms of the phosphate groups are positionally disordered. Details of the structure determination are given in Table 1. Atomic fractional coordinates and thermal parameters are given in Table 4. Selected bond lengths, angles, and nonbonded contacts for **2** are listed in Table 5.

RESULTS AND DISCUSSION

Structure of 1-D $[\text{enH}_2][\text{Zr}(\text{HPO}_4)_3]$, **1**

Compound **1** represents a fundamental structural type for metal phosphates. It is a simple 1-D chain inorganic polymer shown schematically in Fig. 2. The octahedral Zr atoms are bridged by three (HPO_4) groups via $\text{Zr}-\text{O}-\text{P}-\text{O}-\text{Zr}$ linkages. Thus each ZrO_6 octahedron shares three phosphate tetrahedra with each of its neighbors on either side, with the Zr located on a crystallographic inversion site. The

TABLE 2
Atomic Coordinates and Equivalent Isotropic Thermal Parameters (\AA^2) for $[\text{enH}_2][\text{Zr}(\text{HPO}_4)_3]$, **1**

Atom	x	y	z	U(eq)
Zr(1)	0.0000	0.5000	0.0000	0.010(1)
P(1)	0.2600(3)	0.5690(2)	0.2934(2)	0.015(1)
P(2)	0.0000	0.3373(2)	0.2500	0.014(1)
O(1)	0.1643(7)	0.5728(4)	0.1415(6)	0.026(2)
O(2)	0.0433(7)	0.3934(4)	0.1350(6)	0.019(2)
O(3)	0.1627(7)	0.5414(4)	0.3967(6)	0.022(2)
O(4)	0.1331(7)	0.2797(4)	0.3242(6)	0.020(2)
H(4)	0.1452	0.2432	0.2580	0.067
O(5)	0.3259(8)	0.6596(4)	0.3353(7)	0.033(3)
O(6)	0.3902(7)	0.5029(6)	0.3064(7)	0.042(3)
H(6)	0.5000	0.5118(115)	0.2500	0.072
N(1)	0.4382(11)	0.3364(7)	0.4161(9)	0.049(4)
H(1A)	0.4952	0.3433	0.5050	0.150
H(1B)	0.4064	0.3897	0.3849	0.150
H(1C)	0.3586	0.3030	0.4242	0.150
C(2)	0.5392(14)	0.2964(8)	0.3314(10)	0.055(5)
H(2A)	0.6335	0.3277	0.3450	0.150
H(2B)	0.5619	0.2379	0.3635	0.150

polymer chain² is shown with labeling scheme in Fig. 3. In some ways it can be compared to the known 1-D polymers for aluminophosphates $[\text{AlP}_2\text{O}_8\text{H}_x]^{3-x}$ (10, 11), which have tetrahedral Al centers spanned by two phosphate bridges to each neighbor in a manner similar to **1** (Fig. 2a).

There are three crystallographically independent Zr–O bonds in the range 2.044(6)–2.091(6) \AA , the P–O(bridging) distances are 1.517–1.520(6) \AA and slightly shorter than the P–O(terminal) bond lengths of 1.531(6)–1.535(8) \AA . Although the esd's are rather high, the terminal P–O bond lengths would seem to support the formulation $[\text{Zr}(\text{HPO}_4)_3]$ for the inorganic component, with scrambling/disorder of terminal P–OH and P–O[−]/P=O functionalities. In cases where ordering is present, the terminal P–OH bond is normally about 1.59 \AA and terminal P–O/P=O is slightly shorter than bridging P–O bonds, or about 1.50 \AA , due to enhanced d–p π -bonding.

The location of the hydrogen atoms in the structure is also not definitive, though the electron density peaks found would imply a formulation $[\text{Zr}(\text{PO}_4)(\text{HPO}_4)(\text{H}_2\text{PO}_4)]$. Internuclear separations corresponding to possible H-bond contacts are listed in Table 3. These include two short O–O distances, O(4)–O(5) and O(6)–O(6), which involve the terminal P–O oxygen atoms.

If one proton is associated with each of these and is statistically scrambled over both sides of a double well, then

² We are grateful to a referee for bringing our attention to the fact that a compound of formula $[\text{Zr}(\text{HPO}_4)(\text{H}_2\text{PO}_4)_2]$ with cell dimensions $a = 9.84$, $b = 8.25$, $c = 12.88$ \AA , $\beta = 103^\circ$ has been described previously. This might be related to **1** with the (en) groups removed (22).

TABLE 3
Distances and Angles for $[\text{enH}_2][\text{Zr}(\text{HPO}_4)_3]$, **1**

a) Bond lengths (\AA)			
Zr(1)–O(1)	2.091 (6)	Zr(1)–O(2)	2.070 (6)
Zr(1)–O(2) ^a	2.070 (6)	Zr(1)–O(3) ^b	2.044 (6)
P(1)–O(1)	1.517 (6)	P(1)–O(3)	1.520 (7)
P(1)–O(6)	1.535 (8)	P(2)–O(2)	1.517 (6)
P(2)–O(2) ^c	1.517 (6)	P(2)–O(4) ^c	1.531 (6)
C(2)–C(2) ^d	1.561 (18)	N(1)–C(2)	1.481 (16)
b) Bond angles ($^\circ$)			
O(1)–Zr(1)–O(2)	90.7(2)	O(1)–Zr(1)–O(1) ^a	180.0(1)
O(2)–Zr(1)–O(1) ^a	89.3(2)	O(1)–Zr(1)–O(2) ^a	89.3(2)
O(2)–Zr(1)–O(2) ^a	180.0(1)	O(1) ^a –Zr(1)–O(2) ^a	90.7(2)
O(1)–Zr(1)–O(3) ^b	90.1(2)	O(2)–Zr(1)–O(3) ^b	90.1(2)
O(1) ^a –Zr(1)–O(3) ^b	89.9(2)	O(2) ^a –Zr(1)–O(3) ^b	89.9(2)
O(1)–Zr(1)–O(3) ^c	89.9(2)	O(2)–Zr(1)–O(3) ^c	89.9(2)
O(1) ^a –Zr(1)–O(3) ^c	90.1(2)	O(2) ^a –Zr(1)–O(3) ^c	90.1(2)
O(3) ^b –Zr(1)–O(3) ^c	180.0(1)	O(1)–P(1)–O(3)	110.5(4)
O(1)–P(1)–O(5)	108.6(4)	O(3)–P(1)–O(5)	109.2(4)
O(1)–P(1)–O(6)	111.2(4)	O(3)–P(1)–O(6)	107.6(4)
O(5)–P(1)–O(6)	109.7(4)	O(2)–P(2)–O(4)	111.4(3)
O(2)–P(2)–O(2) ^c	110.8(5)	O(4)–P(2)–O(2) ^c	107.0(3)
O(2)–P(2)–O(4) ^c	107.0(3)	O(4)–P(2)–O(4) ^c	109.2(5)
O(2) ^c –P(2)–O(4) ^c	111.4(3)	Zr(1)–O(1)–P(1)	140.1(4)
Zr(1)–O(2)–P(2)	149.4(4)	P(1)–O(3)–Zr(1) ^e	168.8(3)
N(1)–C(2)–C(2) ^d	110.6(11)		
c) Non-bonded contacts			
O(4)–O(5) ^f	2.476	H(4)–O(5) ^f	1.62
O(6)–H(6)	1.23	N(1)–O(4)	2.826
N(1)–O(5) ^g	2.813	N(1)–O(6)	2.764
H(1A)–O(5) ^g	1.96	O(6)–O(6) ^d	2.455
		H(1C)–O(4)	2.07
		H(1B)–O(6)	1.89

Note. Symmetry generated atoms: ^a $-x, 1-y, -z$; ^b $x, 1-y, z-0.5$; ^c $-x, y, 0.5-z$; ^d $1-x, y, 0.5-z$; ^e $x, 1-y, z+0.5$; ^f $0.5-x, y-0.5, 0.5-z$; ^g $1-x, 1-y, 1-z$.

the original formulation of three monohydrogenphosphates is maintained. In fact, one peak of electron density is found on the two-fold axis between the two O(6) atoms at a distance of 1.23 \AA to both. In the case of the O(4)–O(5) interaction, a well-located peak about 0.9 \AA from O(4) and 1.63 \AA from O(5) is found. Since P(2) has two terminal O(4) atoms, this would formally give rise to a (H₂PO₄) functionality, with the other two phosphate groups thus sharing the third proton.

The ³¹P nmr spectrum gives peaks at -8.9 and -14.4 ppm in ratio 1:2, which correspond to P(2) and P(1) respectively. The resonances for the (PO₄), (HPO₄), and (H₂PO₄) groups in α -ZrP and γ -ZrP are at -27.4 , -18.7 , and -9.4 ppm (12). The values for **1** are shifted slightly downfield from what would be expected on average, but the spectrum shows that P(1) and P(2) have different degrees of protonation, due to the uneven occupation of the hydrogen bond double well between O(4) and O(5). Since the protonation states must lie between (H₂PO₄) and (H_{0.5}PO₄), the simplified formulation $[\text{enH}_2][\text{Zr}(\text{HPO}_4)_3]$ is used throughout this paper. This also gives a clearer indication

TABLE 4
Atomic Coordinates and Equivalent Isotropic Thermal Parameters for (\AA^2) for $0.5[\text{enH}_2][\text{Zr}(\text{PO}_4)(\text{HPO}_4)]_2$

Atom	x	y	z	$U(\text{eq})$
Zr(1)	0.6841(1)	0.4500(3)	0.5000	0.006(1)
P(1)	0.7793(1)	-0.0563(9)	0.5000	0.009(1)
P(2)	0.5872(2)	0.9577(9)	0.5000	0.012(1)
O(1)	0.7389(4)	0.1595(19)	0.5000	0.019(3)
O(2)	0.7474(4)	0.6975(17)	0.5000	0.013(3)
O(3)	0.6827(3)	0.4576(12)	0.1855(7)	0.014(2)
O(4)	0.6280(4)	0.7430(19)	0.5000	0.020(4)
O(5)	0.6176(4)	0.2050(17)	0.5000	0.018(3)
O(6)	0.5503(5)	0.9376(29)	0.3114(8)	0.025(3)
H(6)	0.5000	1.0000	0.3114	0.042
N(1)	0.5738(5)	0.6164(23)	0.0000	0.033(5)
H(1A)	0.5830	0.6587	-0.1265	0.079
H(1B)	0.6037	0.5489	0.0599	0.079
H(1C)	0.5620	0.7505	0.0687	0.079
C(2)	0.5272(6)	0.4397(34)	0.0000	0.036(5)
H(2)	0.5301	0.3353	0.1164	0.076

that the three phosphates are effectively in structurally similar environments.

The (enH_2) cations physically separate the 1-D ZrPO chains, and a view down the chain axis showing the separation of the 1-D chains is given in Fig. 4 as a polyhedral representation. The cations also help to stabilize the structure since the three N-H and three terminal P-O groups, O(4), O(5), and O(6), of the asymmetric unit form three well-defined hydrogen bonds with N-O distances of 2.76–2.83 \AA .

Structure of 2-D $[\text{enH}_2]_{0.5}[\text{Zr}(\text{PO}_4)(\text{HPO}_4)]_2$

Compound **2** crystallized as thin plates, but these were of sufficiently strong diffracting power to yield a structure determination. Consistent with its crystal habit, **2** has a sheet phosphate structure and is formulated as $[\text{enH}_2]_{0.5}[\text{Zr}(\text{PO}_4)(\text{HPO}_4)]$. Although neither unit cells nor space group is correlated, analysis shows that the arrangement is topologically similar to that in $\gamma\text{-ZrP}$, $[\text{Zr}(\text{PO}_4)(\text{H}_2\text{PO}_4)]2\text{H}_2\text{O}$ (Fig. 5b). Thus the structure of **2** can be described as a double sheet, viewed from the side in Fig. 6, which shows the position of the intercalated $[\text{enH}_2]$ groups. This side view is also similar to that for the 1-D double stranded polymer $[\text{enH}_2]_{1.5}[\text{Zr}(\text{PO}_4)(\text{HPO}_4)\text{F}_2]$ (8). In **1**, the 1-D double stranded chains become connected into the 2-D double layer sheet by bridging through (PO_4) oxygens rather than having terminal fluorides.

This view from the side also highlights an important difference from $\gamma\text{-ZrP}$ in terms of the alignment of the hydrogenphosphate groups. In $\gamma\text{-ZrP}$ the dihydrogen phosphates are strongly tilted with respect to the plane of the sheet, whereas in **2** the hydrogenphosphates are more nearly

TABLE 5
Distances and Angles for $0.5[\text{enH}_2][\text{Zr}(\text{PO}_4)(\text{HPO}_4)]_2$

(a) Bond lengths (\AA)					
Zr(1)–O(1)	2.045 (10)	Zr(1)–O(2)	2.024 (10)	Zr(1)–O(3)	2.095 (5)
Zr(1)–O(4)	2.078 (10)	Zr(1)–O(5)	2.075 (9)	Zr(1)–O(3) ^a	2.095 (5)
P(1)–O(1)	1.515 (11)	P(1)–O(2) ^b	1.531 (11)	P(1)–O(3) ^c	1.540 (6)
P(1)–O(3) ^d	1.540 (6)	P(2)–O(4)	1.516 (11)	P(2)–O(6)	1.543 (8)
P(2)–O(5) ^e	1.518 (10)	P(2)–O(6) ^f	1.543 (8)	N(1)–C(2)	1.47 (2)
C(2)–C(2) ^f	1.46 (3)				
(b) Bond angles ($^\circ$)					
O(1)–Zr(1)–O(2)	91.0(4)	O(1)–Zr(1)–O(3)	91.5(2)		
O(2)–Zr(1)–O(3)	90.0(2)	O(1)–Zr(1)–O(4)	179.5(4)		
O(2)–Zr(1)–O(4)	89.5(4)	O(3)–Zr(1)–O(4)	88.5(2)		
O(1)–Zr(1)–O(5)	90.7(4)	O(2)–Zr(1)–O(5)	178.3(4)		
O(3)–Zr(1)–O(5)	90.0(2)	O(4)–Zr(1)–O(5)	88.8(4)		
O(1)–Zr(1)–O(3) ^a	91.5(2)	O(2)–Zr(1)–O(3) ^a	90.0(2)		
O(3)–Zr(1)–O(3) ^a	177.1(4)	O(4)–Zr(1)–O(3) ^a	88.5(2)		
O(5)–Zr(1)–O(3) ^a	90.0(2)	O(1)–P(1)–O(2) ^b	110.0(6)		
O(1)–P(1)–O(3) ^c	110.2(4)	O(2) ^b –P(1)–O(3) ^c	109.9(4)		
O(1)–P(1)–O(3) ^d	110.2(4)	O(2) ^b –P(1)–O(3) ^d	109.9(4)		
O(3) ^c –P(1)–O(3) ^d	106.7(5)	O(4)–P(2)–O(6)	108.6(6)		
O(4)–P(2)–O(5) ^e	110.9(6)	O(6)–P(2)–O(5) ^e	109.8(6)		
O(4)–P(2)–O(6) ^a	108.6(6)	O(6)–P(2)–O(6) ^a	109.0(8)		
O(5) ^e –P(2)–O(6) ^a	109.8(6)	Zr(1)–O(1)–P(1)	179.8(2)		
Zr(1)–O(2)–P(1) ^e	161.2(6)	Zr(1)–O(3)–P(1) ^e	142.3(4)		
Zr(1)–O(4)–P(2)	179.7(7)	Zr(1)–O(5)–P(2) ^b	158.2(6)		
N(1)–C(2)–C(2) ^f	113.4(19)				
(c) Non-bonded contacts					
O(6)–O(6) ^h	2.514	O(6)–H(6)	1.26	N(1)–O(3)	3.022
H(1B)–O(3)	2.13	N(1)–O(6)	2.759	H(1A)–O(6)	2.09
H(1C)–O(6)	1.93				

Note. Symmetry generated atoms: ^a $x, y, 1-z$; ^b $x, y-1, z$; ^c $1.5-x, y-0.5, 0.5-z$; ^d $1.5-x, y-0.5, z+1$; ^e $x, y+1, z$; ^f $1-x, 1-y, -z$; ^g $1.5-x, y+0.5, 0.5-z$; ^h $1-x, 2-y, z$.

parallel with it and aligned with similar groups in the adjacent sheet. Examination of hydrogen bond contacts reveals short O–O distances, $\text{O}(6)\text{--}\text{O}(6) = 2.514 \text{\AA}$. A pair of strong P–O–H–O–P hydrogen bonds is the cause of the alignment of the two (HPO_4) groups. In space group $Pnmm$, all four oxygen atoms involved in this bonding are symmetry-related, and so the hydrogen atom positions are

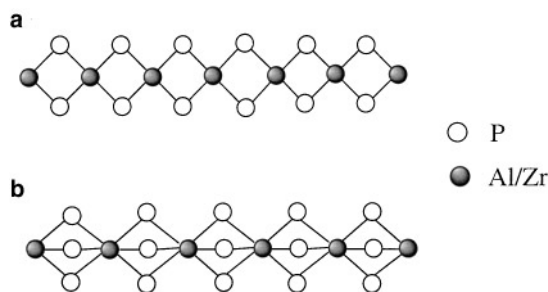


FIG. 2. One-dimensional chain structures for metal phosphates. (a) Double-bridge chain for $[\text{AlP}_2\text{O}_8\text{H}]^{2-}$; and (b) triple-bridge chain for $[\text{Zr}(\text{HPO}_4)_3]^{2-}$ (compound **1**).

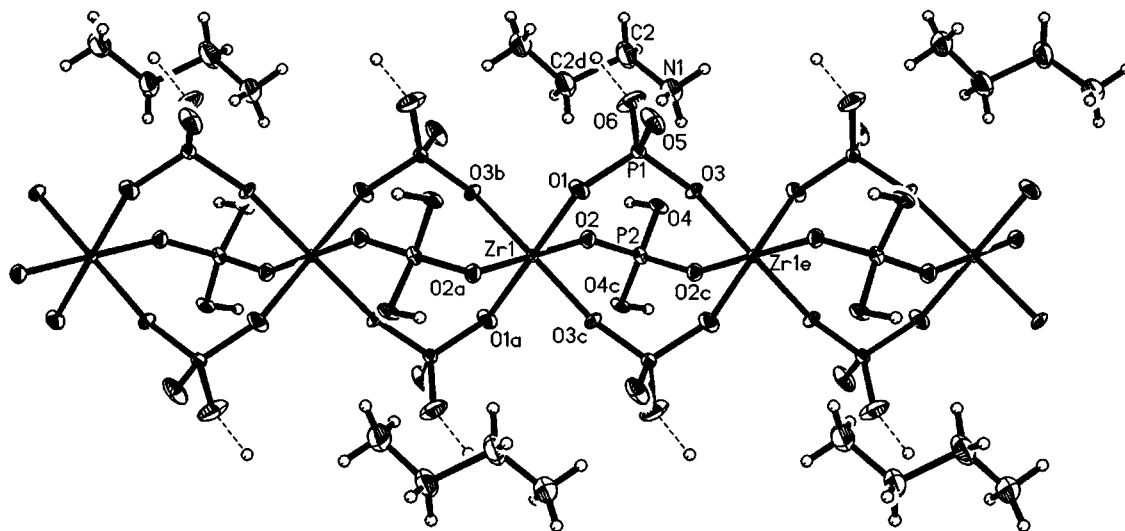


FIG. 3. Compound 1, showing atomic labeling scheme.

assumed to be disordered over all double-well positions. As in the case for **1**, one of the highest residual electron density peaks is found on the two-fold axis midway between the O(6) atoms. The ^{31}P spectrum for **2** (-26.4 and -17.1 ppm) is in close accord with that published for $\text{NH}_4[\text{Zr}(\text{PO}_4)(\text{HPO}_4)]$. This has resonances at -26.0 and -14.7 for the (PO_4) and (HPO_4) groups (13).

The ^{31}P spectrum for **3** also has similar resonances at -24.2 ppm and -19.1 ppm for the phosphate and hydrogen phosphate groups.

The alignment of the (HPO_4) groups in neighboring sheets allows the $[\text{enH}_2]$ ions to fit into the resulting cavities

and to form their own hydrogen bonds, again principally to O(6). These are shown in Fig. 7, along with the atomic labeling scheme for the compound.

The zirconium environment is octahedral, with five independent Zr–O bonds ranging from 2.024 to 2.095 Å, similar to **1**. The P–O bridging distances are normal with the possible exception of P(1)–O(3) 1.540(6) Å, which is slightly longer than expected. This lengthening may be partly due to a weak hydrogen bond formed to O(3) from the organoammonium ion and partly due to the angle $142.3(4)^\circ$ at O(3), which is less than for the other bridging oxygens, with O(1) and O(4) essentially linear (Table 5).

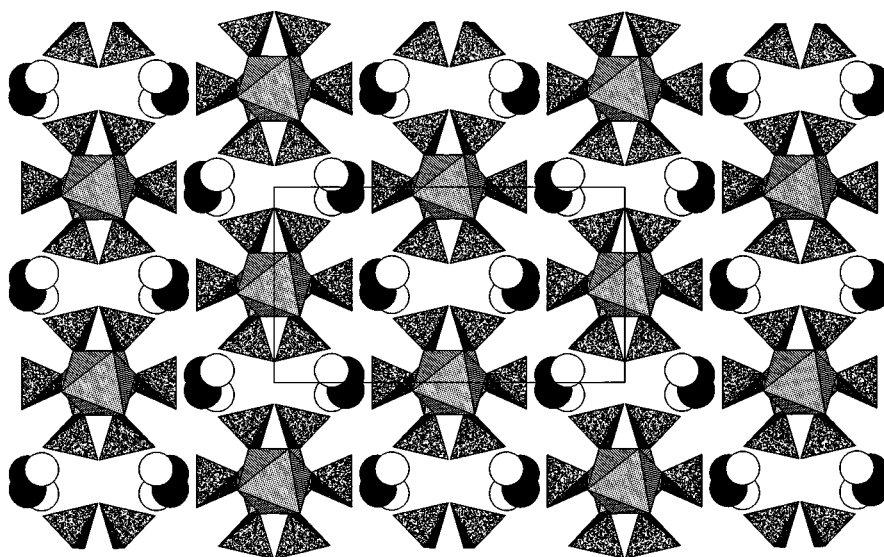


FIG. 4. Compound 1, polyhedral representation, looking down the 1-D chain axis.

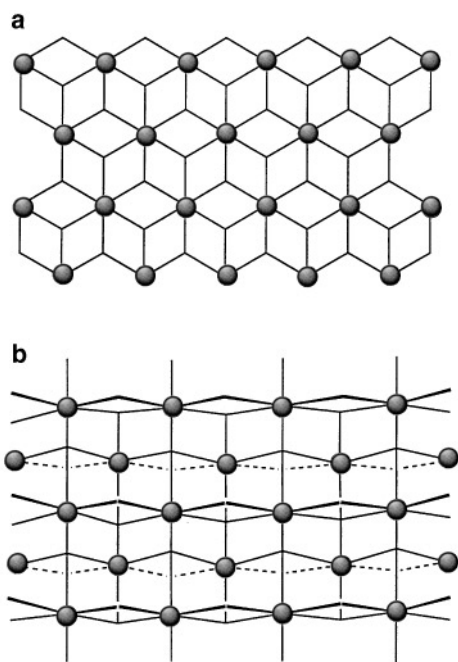


FIG. 5. Two-dimensional zirconium phosphate networks (a) α -ZrP and (b) γ -ZrP, as found for compound **2**.

Compound **2** with its $[\text{enH}_2]$ cations can be related chemically to the ion exchanged phases of α -ZrP and γ -ZrP. In these, protons of the hydrogen phosphate groups are formally replaced by NH_4 , Na, or K cations (13–15). The

structure determination of these phases were often solved by powder X-ray or neutron diffraction, since their formation was usually by direct treatment of the neutral ZrP phase with a basic solution of the cations, which led to disruption of the original large single crystals. The recently solved structure of monoammonium-exchanged phase of γ -ZrP (13) is of special interest for comparison to **2**. Compared to the view of **2** in Fig. 6, each layer in $\text{NH}_4[\text{Zr}(\text{PO}_4)(\text{HPO}_4)]$ is slipped by half a repeat unit along the direction corresponding to b . The (HPO_4) groups are still hydrogen bonded to each other, but make one connection to two different (HPO_4) in the adjacent sheet, rather than two connections to the same, aligned neighbor.

The effect of $[\text{enH}_2]$ on the structure can be seen in this reorganization of the interlayer hydrogen bonds, since two separate and unconnected cavities holding the $[\text{NH}_4]$ ions in the ammonium phase must be merged to accommodate the $[\text{enH}_2]$, which is accomplished by sliding the (HPO_4) groups of adjacent sheets into register with each other.

In addition to direct ion exchange, the lamellar zirconium phosphates have also been the subject of intercalation studies of solvents and organic molecules in place of the interlayer water molecules of the α -ZrP and γ -ZrP structures (16–18). Correlation to the hydrated structures was usually possible, and powder diffraction data were interpreted in terms of expansion of the interlayer spacing due to inclusion of the larger guest molecules. Although in many cases this was reversible, organoamines were found to be irreversibly intercalated, which was attributable to proton transfer and

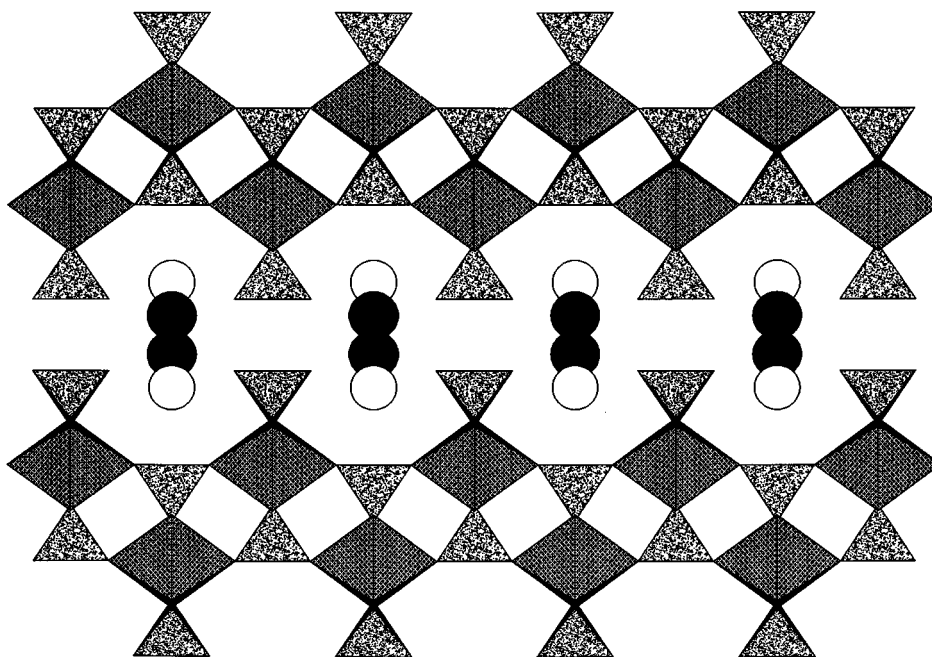


FIG. 6. Compound **2**, side view showing adjacent (HPO_4) groups and intercalation of (enH_2) .

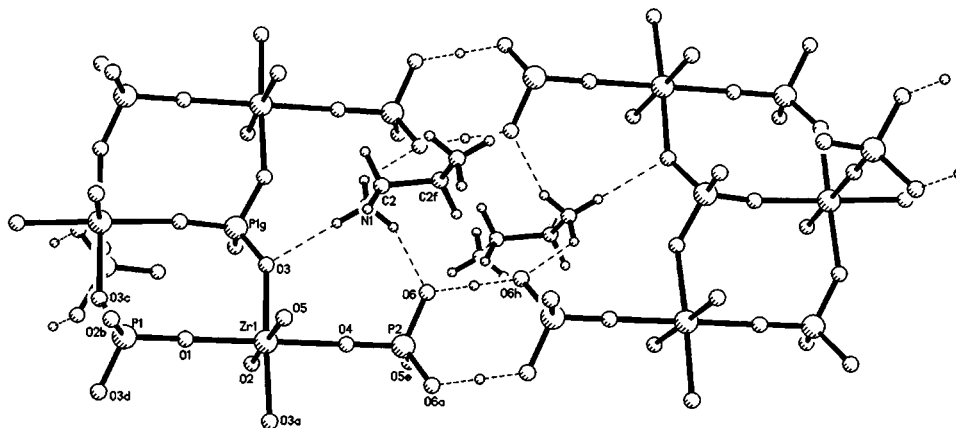


FIG. 7. Compound 2, showing atomic labeling scheme.

the formation of organoammonium ions and negatively charged zirconium phosphate sheets.

Since the adjacent ZrP layers in **2** are in contact through strong hydrogen bonds, this represents a specific structural arrangement, which cannot be readily related to some of the earlier studies of intercalated solvents and amines into α -ZrP or γ -ZrP. In those cases, variation of d-spacing correlating to change in interlamellar separation was found. In

2 the a -axis length is 24.1 Å, which corresponds to a double repeat of sheets, as shown in Fig. 8. Reflection 100 is systematically absent, whereas the 200 reflection with a spacing of 12.04 Å would be expected to be prominent. Thus the “basal spacing” observed for **2** is actually less than that of 12.3 Å found for γ -ZrP itself. In the work of Behrendt *et al.* (16) basal spacings of 13.6–17.8 Å were reported for dmsu, urea, formamide, piperidine, and related molecules intercalated

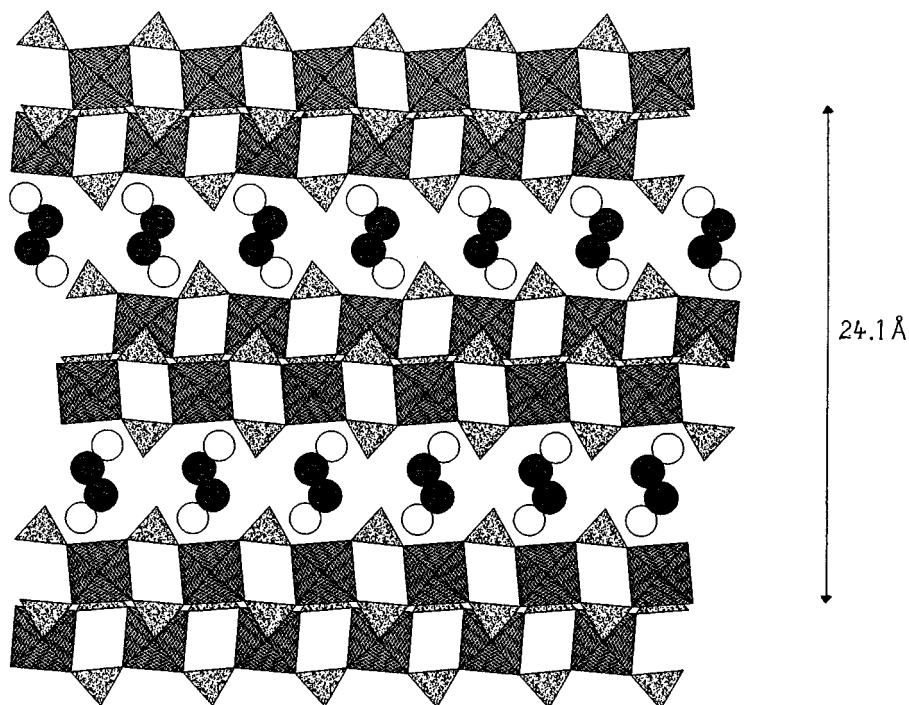


FIG. 8. Alternative polyhedral side view for compound 2, showing axial length repeat.

into γ -ZrP; none of these values can fit with the structure of **2**. Longer chain alkyl ammonium ions, which form large basal spacings, have also been studied by Yamanaka *et al.* (18), however the 23.3 Å value found for hexylamine intercalated into α -ZrP is not related to this current structure.

Formation of **3**

While 2 mol equivalents of HF are required for formation of **1** and **2**, no evidence of the two previously reported fluorinated ZrPO phases was found under these conditions. The use of 8 mol equivalents, however, results in clean formation of fluorinated **3**, which has terminal Zr–F groups. When ZrOCl₂ is used as starting reagent (**9**), less HF may be required for formation of **3** than for the more basic zirconium propoxide, indicating that pH as well as F[−] concentration is critical. Similarly variable results have been found in the indium phosphate system; use of 8 mol equivalents of HF results in formation of the highly fluorinated 3-D open-framework compound 4[*pn*H₂].3[H₃O]. [In₉(PO₄)₈H₂F₁₆].3H₂O (**19**), whereas use of 2.0 mol equivalents HF may or may not lead to F[−] incorporation (**19**, **20**).

Templating Effects

The structures we have found are strongly organized by the packing and hydrogen bond requirements of the organocation. In the case of ethylene diammonium at least four different crystalline phases have been formed, and it is clear that synthesis conditions are quite crucial to the resulting products. In each case, however, the [enH₂] both fits snugly and makes optimal H-bonds to supplement those already existing for the acid phosphate moieties.

To look at the “template effect” of the cations, we have studied a number of other organoamine templates in the zirconium phosphate system under similar phosphate-rich acidic conditions. From these other studies we also wish to report an interim result that use of imidazole, (Im = C₃N₂H₄) as the organic template gives a novel salt intercalate [ImH][Zr(HPO₄)₂]₂[H₂PO₄].³ This has a zirconium phosphate sheet of the α -type, in which each octahedral Zr is connected to six (HPO₄) groups and each hydrogen phosphate is connected to three Zr atoms, with the P–OH functionalities pendant to the sheet (Fig. 5a). In this case two formula units of the sheet are intercalated by a dihydrogen-phosphate anion and an imidazolium cation, which is badly disordered, rather than two molecules of water as would be

the case for α -ZrP itself. Thus a phosphorus rich phase, this time with Zr:P 2:5 can be found in this system. Further work on this and related systems seems likely to give more interesting results in which organic and inorganic moieties are matched to give novel structures and arrangements.

CONCLUSIONS

Phosphate-rich gels yield the new organically templated phases 1-D [enH₂][Zr(HPO₄)₃] and 2-D [enH₂]_{0.5}[Zr(PO₄)(HPO₄)] when 2.0 mol equivalents of fluoride are used. The 1-D compound represents a new structural type with chains of Zr polyhedra connected through three bridging hydrogen phosphate groups. The 2-D compound is related to γ -ZrP and previously studied amine intercalates.

If a larger quantity of HF is employed in the synthesis, a high yield of the 3-D microporous fluorinated zirconium phosphate [enH₂]_{0.5}[Zr₂(PO₄)₂(HPO₄)F].H₂O in a phase-pure form can be obtained. In contrast to certain classical cases involving zirconium phosphates, single crystals large enough for X-ray structure determination have been obtained in each case by the fluoride-assisted hydrothermal synthetic approach.

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REFERENCES

1. A. Clearfield, *Solid State Ionics* **46**, 35 (1991).
2. P. R. Rudolf, M. A. Subramanian, A. Clearfield, and J. D. Jorgensen, *Solid State Ionics* **17**, 337 (1985).
3. J. M. Troup and A. Clearfield, *Inorg. Chem.* **16**, 3311 (1977).
4. G. Alberti, M. Casciola, V. Constantino, and M. Leonardi, *Solid State Ionics* **14**, 289 (1984).
5. D. M. Poojary, B. Shpeizer, and A. Clearfield, *J. Chem. Soc., Dalton Trans.* 111 (1995).
6. D. M. Poojary and A. Clearfield, *Inorg. Chem.* **33**, 3685 (1994).
7. D. M. Poojary, L. A. Vermeulen, E. Vicenzi, A. Clearfield, and M. E. Thompson, *Chem. Mater.* **6**, 1845 (1994).
8. M. B. Hursthouse, K. M. A. Malik, J. M. Thomas, J. Chen, J. Xu, T. Song, and R. Xu, *Russ. Chem. Bull.* **43**, 1787 (1994).
9. E. Kennitz, M. Wloka, S. Trojanov, and A. Stiewe, *Angew. Chem. Int. Ed. Engl.* **35**, 2677 (1996).
10. I. D. Williams, J. Yu, Q. Gao, J. Chen, and R. Xu, *Chem. Commun.* 1273 (1997).
11. R. H. Jones, J. M. Thomas, R. Xu, A. K. Cheetham, and D. Bieber, *J. Chem. Soc., Chem. Commun.* 170 (1990).
12. N. J. Clayden, *J. Chem. Soc. Dalton Trans.* 1877 (1987).
13. D. M. Poojary, B. Zhang, Y. Dong, G.-Z. Peng, and A. Clearfield, *J. Phys. Chem.* **98**, 13616 (1994).
14. P. R. Rudolf and A. Clearfield, *Inorg. Chem.* **28**, 1706 (1989).

³Crystal data for [ImH][Zr(HPO₄)₂]₂[H₂PO₄]; C₃H₁₁N₂O₂₀P₅Zr₂, monoclinic, space group C2/m, *a* = 21.450(6), *b* = 5.428(2), *c* = 9.134(2) Å, β = 97.22(2)°, *V* = 1055.2(5) Å³, *R* = 0.034, *wR* = 0.038 for 986 reflections (*F* ≥ 4 σ (*F*)).

15. A. Clearfield, L. B. McCusker, and P. R. Rudolf, *Inorg. Chem.* **23**, 4679 (1984).
16. D. Behrendt, K. Beneke, and G. Lagaly, *Angew. Chem. Int. Ed. Engl.* **15**, 544 (1976).
17. E. Michel and A. Weiss, *Z. Naturforsch. B: Condens. Matter* **22**, 1100 (1967).
18. S. Yamanaka, J. Haribe, and M. Tamake, *J. Inorg. Nucl. Chem.* **38**, 323 (1976).
19. I. D. Williams, J. Yu, H. Du, J. Chen, and W. Pang, *Chem. Mater.* **10**, 773 (1998).
20. H. Du, J. Chen, W. Pang, J. Yu, and I. D. Williams, *Chem Commun.* 781 (1997).
21. G. M. Sheldrick, "Shelxtl-Plus," Siemens Analytical Instruments, (1993).
22. E. Torraca and G. Alberti, in "Ion Exchange in the Process Industry," p. 315. Society of Chemical Industry, London, 1970.